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Impact of particle formation on atmospheric ions and particle number concentrations in an urban environment

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Abstract

A measurement campaign was conducted from 3 to 19 December 2012 at an urban site of Brisbane, Australia. Size distribution of ions and particle number concentrations were measured to investigate the influence of particle formation and biomass burning on atmospheric ion and particle concentrations. Overall ion and particle number concentrations during the measurement period were found to be (-1.2 x 10^3 cm^{-3} | +1.6 x 10^3 cm^{-3}) and 4.4 x 10^3, respectively. The results of correlation analysis between concentrations of ions and nitrogen oxides indicated that positive and negative ions originated from similar sources, and that vehicle exhaust emissions had a more significant influence on intermediate/large ions, while cluster ions rapidly attached to larger particles once emitted into the atmosphere. Diurnal variations in ion concentration suggested the enrichment of intermediate and large ions on new particle formation event days, indicating that they were involved in the particle formation processes. Elevated total ions, particularly larger ions, and particle number concentrations were found during biomass burning episodes. This could be due to the attachment of cluster ions onto accumulation mode particles or production of charged particles from biomass burning, which were in turn transported to the measurement site. The results of this work enhance scientific understanding of the sources of atmospheric ions in an urban environment, as well as their interactions with particles during particle formation processes.

Keywords: Atmospheric ions; Biomass burning; New particle formation

Highlights:

1. Concentration and size distribution of atmospheric ions were measured
2. Transport contributes to large ions but enhances sink of cluster ions in urban areas
3. Atmospheric ions involved in new particle formation processes in urban areas

1. Introduction

Atmospheric ions are mainly formed by the ionization of air molecules by cosmic rays from space, or alpha radiation from natural radioactive materials such as Rn-222 in the ground and its airborne progeny (Reiter 1992). In addition, an increase in cluster ion concentration has also been observed during nucleation events in boreal environments (Vana et al., 2006). Moreover, ions are known to be emitted from combustion processes, hot surfaces and flames (Maricq, 2006; Fialkov, 1997; Peineke and Schmidt-Ott, 2008), as well as during the break-up of water droplets (Laakso et al., 2007). In urban environments, vehicle emissions are the major source of many pollutants including ions and charged particles. Cluster ion concentration (< 2 nm) measured near roadside and motorway sites has been found to be several times higher than that in the urban background (Jayaratne et al., 2010).

Previous studies of ion measurements have focused on contribution of ions (i.e. ions induced nucleation, IIN) to the particle formation process in rural areas (e.g., Laakso et al., 2004; Hirsikko et al., 2007), whereas limited studies have been conducted in urban environments (Hirsikko et al., 2011). In an urban setting, particle sources are more complex than those in rural areas due to the mixing of different combustion emissions, such as those from transportation (e.g. motor vehicles, ships and aircraft), industrial sources, power plants, and occasionally biomass burning and eolian dust particles from rural areas (Morawska et al., 2008; González and Rodríguez 2013). Different sources have their own pollution characteristics which interact with each other, thereby making it difficult to interpret the resulting data in relation to the physico-chemical properties and formation mechanisms. Elevated particle number concentration (PNC) associated with new particle formation (NPF) events has been frequently observed in Brisbane during the warm season (Cheung et al., 2011). Kalivitis et al. (2012) found a negative correlation between cluster ion and black carbon concentrations where the loss of cluster ions were due to ion attachment on the accumulation particles associated to the black carbon source in the study area. Although the characterization of atmospheric particles associated with NPF and biomass burning has been studied, very few reports were made pertaining to ions and charged particles. The study of atmospheric ions is vital, not only due to their potential impacts on human health, but also their involvement in atmospheric particle formation processes (Fews et al., 1999; Henshaw 2002; Hirsikko et al., 2007).

The aim of this study was to investigate the influence of NPF and biomass burning on the variation of atmospheric ion and particle number concentrations in an urban environment. In this paper, we present the size distribution of ions and PNC measured in an urban area of Brisbane, Australia. New particle formation and the transport of biomass burning emissions from upwind of the site were both observed in the study area where ambient levels of ion and aerosol particles were elevated. To our knowledge, this is the first report on the variations of ion size distribution under the influence of biomass burning in an urban environment. The results enhance our understanding of the sources of atmospheric ions and their interactions with particles during the particle formation process.

2. Methodology

2.1 Study design

The measurements were conducted at the International Laboratory for Air Quality and Health (ILAQH), Queensland University of Technology (QUT) (see **Fig. 1** for map). The monitoring site was about 10 m a.g.l. on the top floor of a QUT campus building, which lies to the south of the city center, with a major highway (the Pacific Motorway) carrying about 120,000 motor vehicles per day situated about 100 m away along the southwest of the site. The other major sources of air pollutants in Brisbane include the airport, oil refinery and Port of Brisbane located about 10 km to the northeast of the campus, and a gas-fired power plant located about 40 km to the southwest of the sampling site. Therefore, the pollution associated with the northeasterly winds could be mainly attributed to industrial and aircraft/ship emissions, while that associated with southerly to northwesterly winds was due mostly to local traffic exhaust emissions in addition to the plumes of power plant.

Monitoring was conducted from 3 to 19 December 2012, when nucleation events were most likely to occur (Cheung et al, 2011). Furthermore, controlled burning generally continued around Brisbane at this time of the year and we wished to investigate the effect of biomass burning emissions on the ion concentrations. In the context, the results of this investigation should be attributed generally to the characteristics of ions and aerosols for biomass burning season in Brisbane. During the sampling period, prevailing synoptic winds in the Brisbane area were from the northeast, except from 10 to 15 December, when southeasterly winds dominated. During the study period, the mean temperature was observed to be 27 °C, with minimum and maximum temperatures of 18.9 °C and 41.9 °C, respectively. A light breeze (~1-3 m s^{-1}) was generally observed, with light precipitations on 8^{th} (0.6 mm), 10^{th} (0.6 mm), 11^{th} (5.4 mm) and 19^{th} (1 mm) of December.

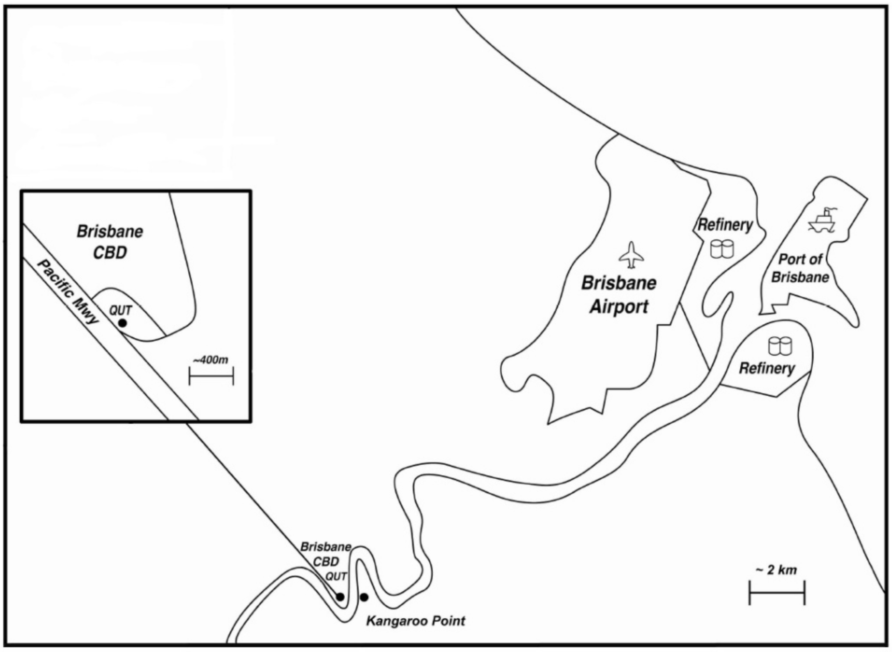

Figure 1. Geographical locations of the monitoring site of this study and the major air pollution sources in the Brisbane.

2.2 Measurement techniques

The size distribution of ions, charged and neutral particles were measured by a Neutral cluster and Air Ion Spectrometer (NAIS, Airel Ltd.) at the QUT monitoring site. The detection size range of the instrument was from 0.8 to 42 nm for both ions and particles. The NAIS consisted of two identical electrical mobility analyzer columns, one for each polarity, so that ions of both signs could be monitored simultaneously. The aerosols were size-classified by the mobility analyzers and measured with an array of 21 electrometers in each column. The air sample was drawn into the NAIS from outside the building through a 2.54 cm (inner diameter) conductive rubber tube with a length of 1100 mm, at a sampling flow rate of 60 Lpm

(30 Lpm in each column). The instrument is designed to sample in a cycle and the sampling duration was set to 2 min per sample. PNC was continuously measured by a Condensation Particle Counter (CPC, TSI 3787) which counted total number of particles from the size range of ≥ 5 nm. The sample was drawn through a 6.35 mm (inner diameter) conductive rubber tube and the data time resolution was 1 min. Sulfur dioxide concentration (SO_2) was measured by a pulsed UV fluorescence analyzer (Ecotech 9850, with a detection limit of 0.5 ppbv and accuracy of ±1% of instrument reading) with a sampling interval of 5 min. Span and zero calibrations were conducted before and after the study.

In addition, carbon monoxide (CO), nitrogen dioxide (NO_2) and mass concentration of $PM_{2.5}$ and PM_{10}, as well as meteorological parameters (including wind speed/direction, temperature, relative humidity, and global solar radiation) measured by Queensland Department of the Environment and Heritage Protection (EHP) in the city of Brisbane were used to assist with the data analysis. A detailed description of the instruments used for the acquisition of meteorological data is available at the EHP website (http://www.ehp.qld.gov.au/air/pollution/pollutants/index.html).

2.3 Data processing and analysis

During the sampling period, the NAIS data was found to be affected by emissions from cleaning equipment operated at 06:00 LT on campus during weekdays, therefore the corresponding data (~ 30 - 60 min) was removed from the database. Spurious events also resulted in occasional data spikes on the NAIS. In order to eliminate these, the upper limit of the ion concentrations was set to 10^5 cm^{-3}. Particle diffusional loss through the sampling tube in the NAIS was calculated as ~3 % at 2 nm ion size, thus no diffusional loss corrections were applied to ion concentrations. The ion data were then classified into groups according to size as follows: i) cluster ions (≤ 1.6 nm), ii) intermediate ions (1.6 nm < d ≤ 7 nm), large ions (7 nm < d ≤ 42 nm), and iv) total ions (≤ 42 nm).

3. Results and discussion

3.1 Overall results

During the period of 3 to 15 December 2012, four clear particle formation events were observed, which occurred on 9, 13, 14 and 15 December. During the later stage of the study (16-19 December 2012), a bushfire occurred about 200 km north of the monitoring site. Northerly winds dominated during 16 to 19 December and carried the biomass burning emissions to the study area, resulting in an increase in particulate matter pollution and elevated levels of ions. In this section, we focus our discussion on the variation and possible sources of the ions for the entire study period. The specific influence of NPF and biomass burning on ion and particulate matter concentrations will be discussed in later sections.

The median number concentrations of ions and aerosol particles were found to be -1225 cm^{-3} | +1639 cm^{-3} (total ions), -221 cm^{-3} | +301 cm^{-3} (cluster ions) and 4389 cm^{-3} (PNC), respectively (- / + signs are used to represent the negative / positive polarities of ions) (see **Table 1**). The ion concentrations are similar to those measured in other urban areas, such as the Yangtze River Delta, China (median: 770 cm^{-3} for total ions, Herrmann et al., 2013) and Kuopio, Finland (mean: -320 cm^{-3}| +280 cm^{-3} for cluster ions, Titta et al., 2007).

Table 1. Summary of the number concentration of cluster and total ions, and PNC for various periods throughout this study.

Period	Parameters	Median	S.D.	95% percentile	5% percentile	Sample no.
Whole period (3 – 19 Dec 2012)	**-ve cluster ions (cm^{-3})**	221	65	327	102	406
	+ve cluster ions (cm^{-3})	301	90	426	130	406
	-ve total ions (cm^{-3})	1225	667	2472	867	406
	+ve total ions (cm^{-3})	1639	2586	3450	1178	406
	PNC (cm^{-3})	4389	10194	17290	1516	379
3 – 15 Dec 2012	**-ve cluster ions (cm^{-3})**	232	56	330	148	310
	+ve cluster ions (cm^{-3})	316	75	432	162	310
	-ve total ions (cm^{-3})	1195	576	2256	857	310
	+ve total ions (cm^{-3})	1634	671	2590	1176	310
	PNC (cm^{-3})	4144	9645	12612	1345	283
16 – 19 Dec 2012	**-ve cluster ions (cm^{-3})**	178	71	280	39	96
	+ve cluster ions (cm^{-3})	228	91	363	53	96
	-ve total ions (cm^{-3})	1376	859	2965	956	96
	+ve total ions (cm^{-3})	1656	5024	12036	1246	96
	PNC (cm^{-3})	5570	11447	26769	2302	96

The cluster ion data were classified further into daytime (08:00 – 16:00) and nighttime (20:00–04:00) sub-groups. The nighttime interval was chosen in order to remove the influence of photochemical reactions that were prevalent during daylight hours. Positive and negative cluster ions were found to be well correlated (r: 0.91 - 0.93; $p < 0.01$) with a slope value of 0.66 and 0.68 for daytime and nighttime, respectively (see **Figure 2a-b**). With similar charge ratios, these results suggested that both negative and positive ions were generated from the same source or sources, and the influence of photochemical reactions on the ion charge balance was limited.

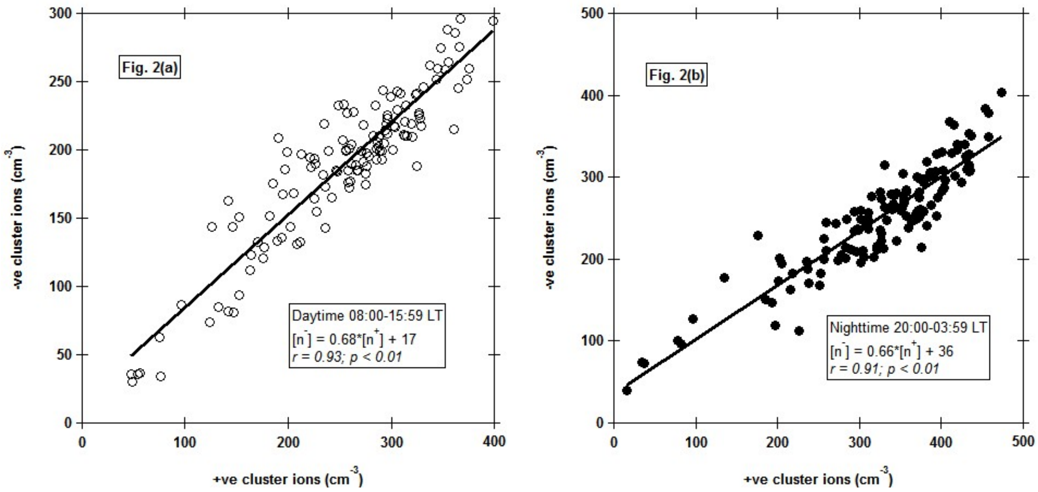

Figure 2. Scatter plots of negative and positive cluster ions during (a) daytime and (b) nighttime.

Since nitrogen oxides is an indicator of vehicle exhaust emissions in urban environments (Cheung et al., 2013), the relationship between ion concentrations and NO_2 mixing ratios was examined to study the influence of local vehicle emission on the former. **Figure 3(a-c)** illustrates the correlation between the total concentrations (sum of negative and positive polarities) of a) cluster ions, b) intermediate ions and c) large ions against NO_2 during the nighttime. Because the influence of photochemical production was negligible during the nighttime, ions were mostly produced by local vehicle exhaust emissions and/or other natural sources. A negative correlation was found between cluster ions and NO_2, while positive correlations were found between large ions and NO_2 (r: 0.65, p<0.01). Similar patterns were found between ion concentrations and PNC (see **Figure 4(a-c)**). These findings suggested that vehicle exhaust emissions contained large ions and particles, which could enhance the coagulation sink of cluster ions and be a possible cause of the negative correlation found between cluster ions and NO_2/PNC, whereas a positive correlation was found for large ions (Cheung et al., 2013; Jayaratne et al. 2013).

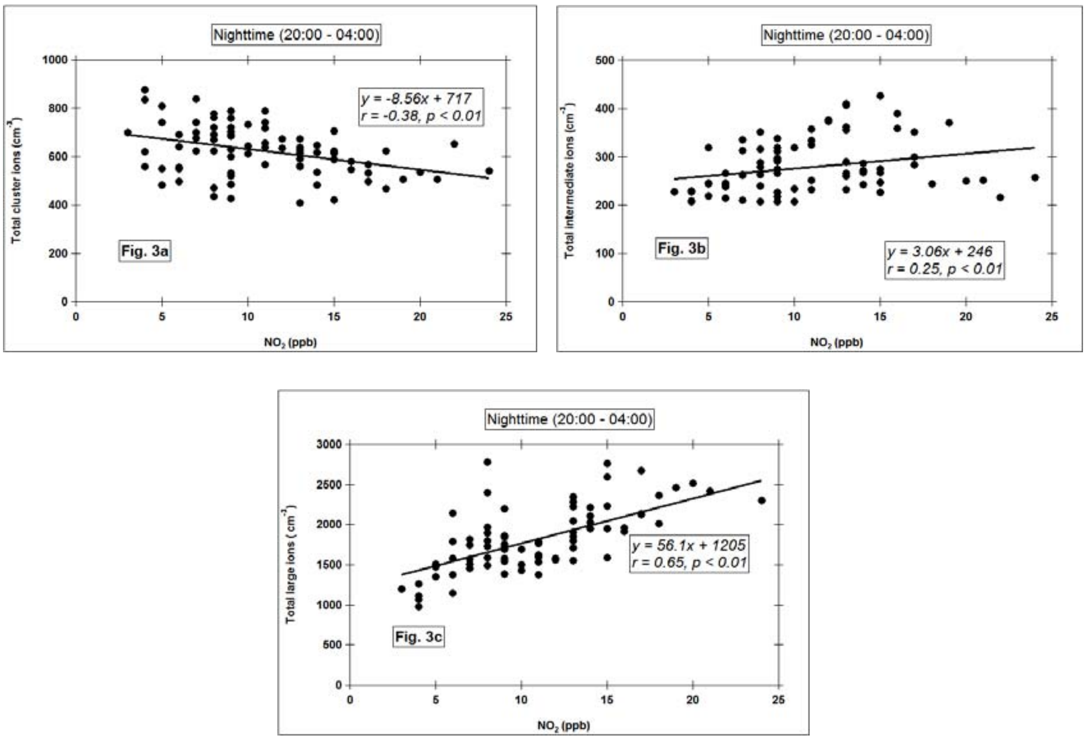

Figure 3(a-c). Scatterplots between the total concentrations of a) cluster ions, b) intermediate ions and c) large ions and NO_2 at nighttime (20:00 – 04:00 LT).

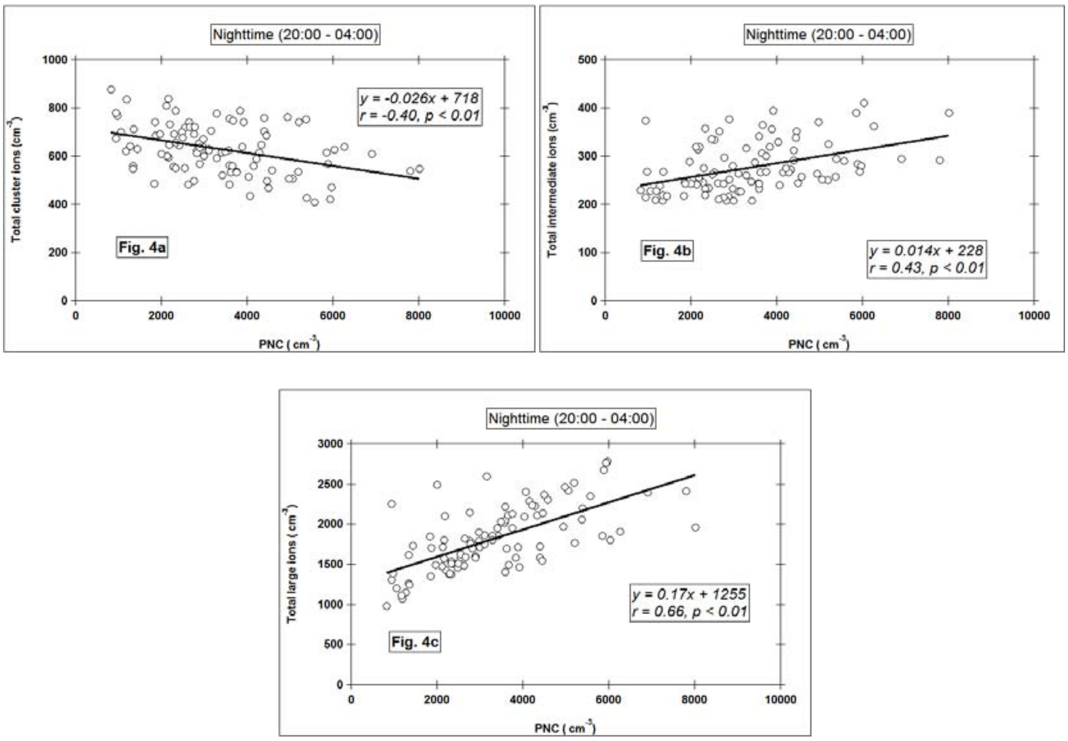

Figure 4(a-c). Scatterplots between the total concentrations of a) cluster ions, b) intermediate ions and c) large ions and PNC at nighttime (20:00 – 04:00 LT).

Figure 5(a-c) shows the wind rose plots for a) cluster ions, b) intermediate ions and c) large ions. For cluster and intermediate ions, relatively weak directional dependency was observed compared to that for large ions. In previous studies, anthropogenic pollution (including local vehicle and industrial emissions) was found to be dominant when southwesterly and northeasterly winds prevailed (Cheung et al., 2011, 2012). The results of this study further suggested that higher large ion concentrations were also associated with the southwest / northeast directions, whereas the relatively uniform concentrations for cluster and intermediate ions were attributed to neutral ion production, such as the ionization of air molecules by cosmic rays. Although vehicle exhaust emissions were found to be a major source of cluster ions in urban areas (Ling et al., 2010), their concentration fell to the background level within about 20 meters from their sources (Jayaratne et al., 2010). Thus, considering an approximate distance of 100 meters between major roads and the measurement sites, the impact of vehicle emissions on cluster/intermediate ion concentrations in the atmosphere could be insignificant, with only a slightly positive bias for the cluster ion concentrations associated with a southwesterly direction.

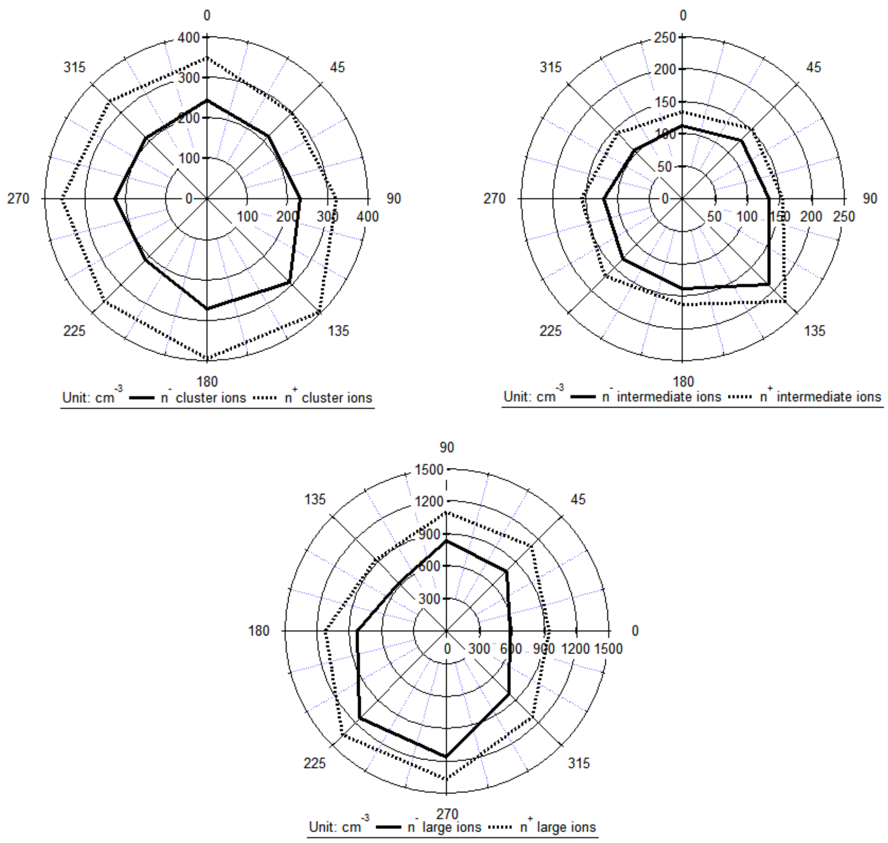

Figure 5. Wind rose plots of a) cluster ions, b) intermediate ions and c) large ions. Solid line: -ve ions, and dash line: +ve ions.

3.2 Influence of new particle formation

The time series plots of ions / charged particles during NPF events are illustrated in **Figure 6**. Although the size distribution of the ions / charged particles did not show a clear “banana” shape (which is a typical feature for particle formation), the increase in intermediate ions can be used as an indicator of particle growth during the sampling day (Hirsikko et al., 2007). A NPF event is defined as the increase of the number concentration of intermediate ions followed by the particle growth from nucleation mode into Aitken mode in a few hours. Four events were observed which were on 9th, 13th, 14th and 15th December 2012. Increase of intermediate ion concentrations were observed at the initial stage of the events and followed by the particle growth into larger sizes which last for a few hours. The ion concentrations measured during NPF event and non-event days are tabulated in **Table 2**. Significantly higher concentrations were found for intermediate ions (19-26 % higher) during NPF events, compared to non-event days, but it was only 7-8 % and 6-8 % higher for cluster and large ions, respectively. It should be noted that two plumes of PNC were observed on 10 December 2012. For the first plume (~07:00 -08:00 LT), the increase of intermediate ions was instantaneous and did not grow gradually to larger ions neither forming the distinct “banana” in the size spectra, therefore this was not classified as a NPF event (see Fig. 6). For the second plume (~13:00 – 16:00 LT), similarly, intermediate ions increased and subsided instantaneously and without undergoing a particle growth process. Therefore, the two plumes observed on 10 December were not defined as NPF event in this study (see Fig. S1 in the supplementary section for details).

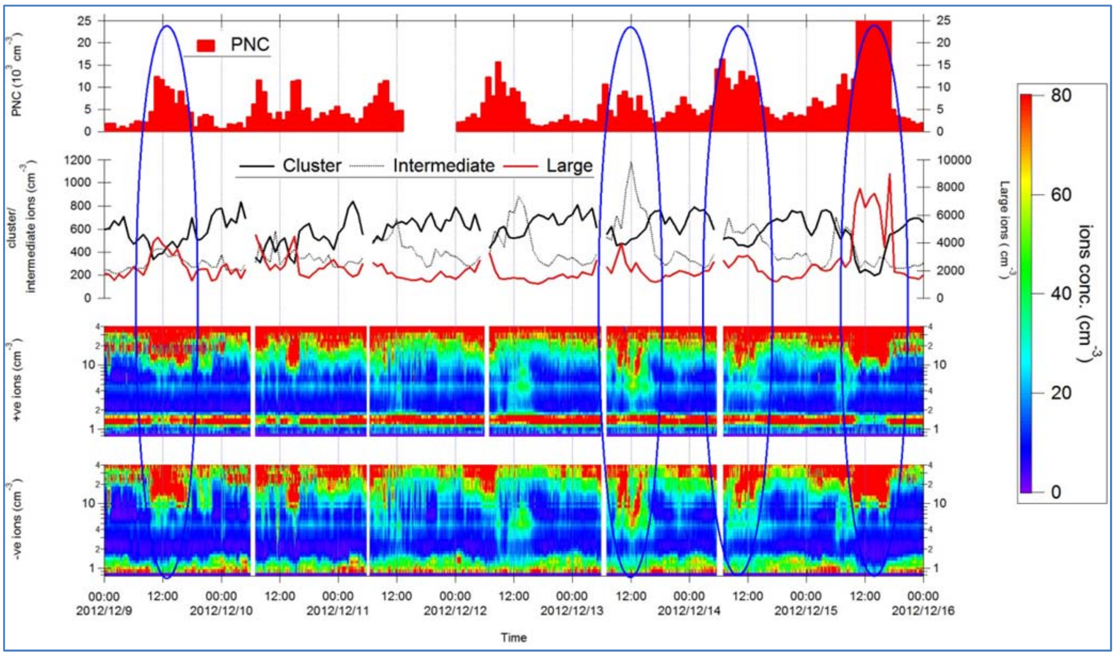

Figure 6. From bottom to top: time series of size distribution of i) negative and ii) positive ions and number concentrations of iii) cluster/ intermediate/ large ions and iv) PNC. NPF events were highlighted as indicated by increases of both intermediate and large ions.

Table 2. Summary of ion concentrations measured during NPF event and non-event days.

	Event days			Non-event days		
	Median	**S.D.**	**No. of data**	**Median**	**S.D.**	**No. of data**
PNC	5046	15542	96	3875	2929	187
-ve cluster ions	246	64	96	228	52	214
-ve intermediate ions	159	95	96	125	65	214
-ve large ions	822	734	96	776	499	214
-ve total ions	1249	693	96	1175	503	214
+ve cluster ions	337	77	96	311	73	214
+ve intermediate ions	184	82	96	153	59	214
+ve large ions	1161	667	96	1067	677	214
+ve total ions	1715	606	96	1573	686	214

Diurnal variations of the negative and positive ions are depicted in **Figure 7**, which shows the temporal variations of the ions on NPF event and non-event days. The results show that there was an increase in ions from the cluster/intermediate to large size range during morning to noontime on the event days (i.e. 08:00 LT for cluster/intermediate ions and 10:00 LT for large ions). Moreover, higher concentrations of intermediate and large ions were observed for event days compared to non-event days (see middle and upper panel of **Figure 7**). In constrast, a lower concentration of cluster ions was found during the noontime (~ 10:00 – 15:00 LT) on event days, which was due to their enhanced attachment to particles which increased during NPF events (Hõrrak et al., 2008). In addition, the relationship between cluster, intermediate and large ion concentrations and the indicator of sulfuric acid production (as represented by the product of SO_2 and solar radiation (SR)) are shown in **Figure 8a-b**. A negative correlation was found for cluster/intermediate ions vs. O_2*SR with *r* values of -0.64 to -0.89 (see **Figure 8a-b**), while a positive correlation was observed between large ions and SO_2*SR (*r*: 0.66; $p < 0.01$, see **Figure 8c**). Also, similar patterns of scatter plots were found between ions and PNC, with *r* values of -0.83 to -0.95 for cluster/intermediate ions and 0.97 for large ions. The increase in PNC with SO_2*SR was shown to be accompanied by a corresponding decrease in cluster/intermediate ions and an increase in large ions. These results suggested that intermediate ions were produced in the earlier stage of NPF events, followed by growth processes which led to the formation of large ions. Moreover, the negative correlations between cluster/intermediate ions and PNC/SO_2*SR suggested that both cluster/intermediate ions were rapidly coagulated with the large particles during particle formation, so that a positive relationship was only obtained between large ions and SO_2*SR. In summary, the results showed that both intermediate and large ions were involved in particle growth and formation processes, which were enhanced with the presence of sulfuric acid.

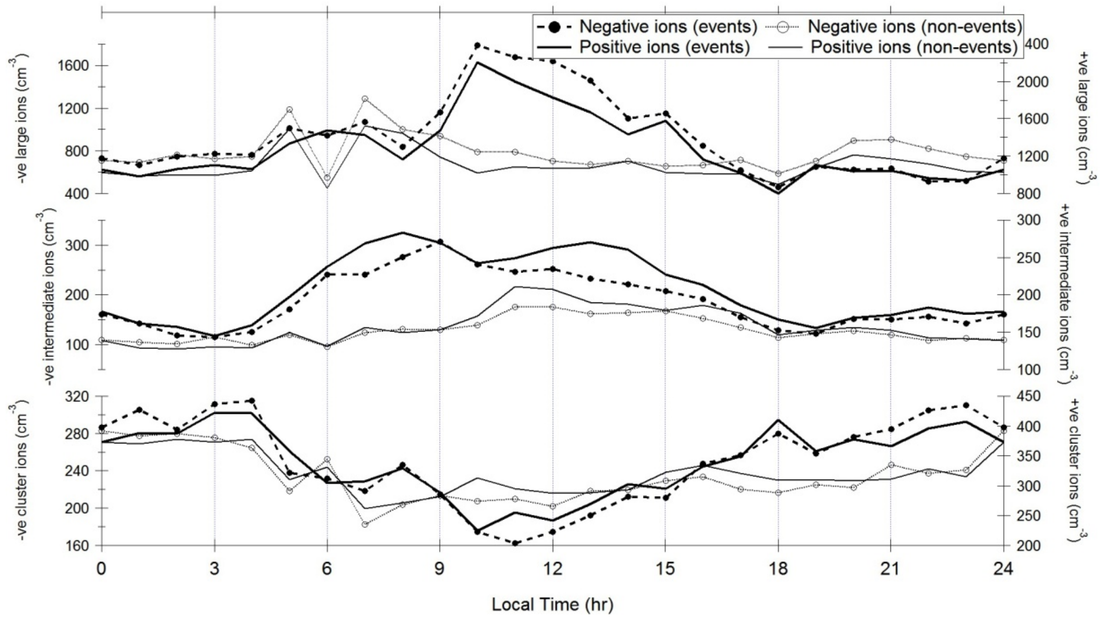

Figure 7. Diurnal variations of negative and positive ions obtained for NPF event days and non-event days. From bottom to top: i) cluster ions, ii) intermediate ions and iii) large ions.

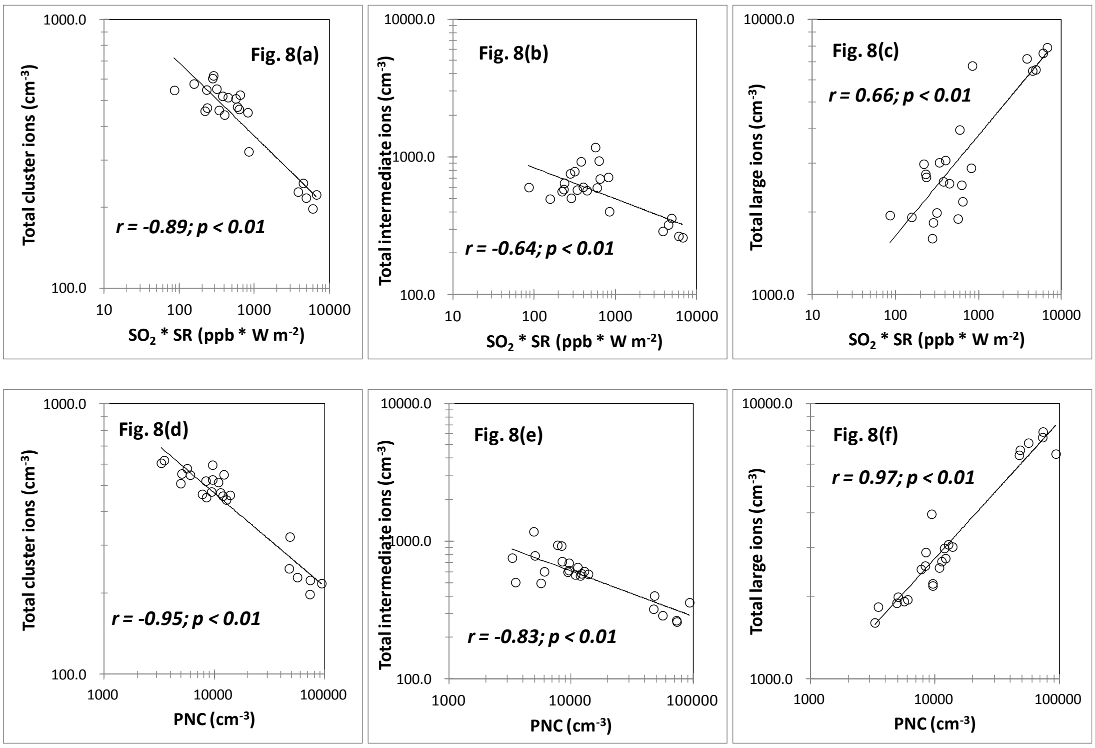

Figure 8(a-f). For upper panel, scatter plots between the total concentrations of a) cluster ions, b) intermediate ions and c) large ions and SO_2*SR during the NPF events. For lower panel, scatter plots between the total concentrations of d) cluster ions, e) intermediate ions and f) large ions and PNC during the NPF events.

3.3 Influence of biomass burning

During the later stage of the measurement period (16 - 19 December 2012), a bushfire occurred about 200 km north of Brisbane. **Figure 9** shows the temporal variations of PM_{10} and wind direction/speed measured at QUT, Mount Creek (MC) and Flinders View (FV) stations. During this period, the transport of PM_{10} was observed from the upwind area of MC to QUT and further downwind to the FV area, as indicated by the predominant northerly winds at all three stations. At the upwind MC station (~100 km north to QUT), PM_{10} reached 60 μg m^{-3} in the evening (~ 23:00) of 16 December 2012. An increase of PM_{10} was then observed at QUT and FV at a later time. The PM_{10} measured at QUT increased from about 20 μg m^{-3} to 55 μg m^{-3}, which was about 2 times higher than that before the impact from biomass burning (i.e. PM_{10} was below 20 μg m^{-3} on 16 December 2012). The influence of biomass burning can also be indicated by the ratio of carbon monoxide to nitrogen dioxides ($\Delta CO/\Delta NO_2$). In general, higher $\Delta CO/\Delta NO_2$ value was found under the influence of biomass burning (~24.6) and lower ratio was observed when vehicle emission is dominant source (~9.7) in Brisbane region (Cheung et al. 2011). During the period of 16 – 19 Dec, relatively higher $\Delta CO/\Delta NO_2$ mixing ratios were obtained during the evening/early morning when the impact of local vehicle emission was minimized during the nighttime (bottom panel of **Figure 9**). The results suggested that the biomass burning contributed to the elevated PM_{10} observed at the measurement site.

A significant increase in total ion concentrations was found on 16-17 December during the biomass burning episode as indicated by the high $\Delta CO/\Delta NO_2$ ratio. On the other hand, the relatively lower concentration of cluster ions was likely due to the recombination of existing cluster ions and their attachment to the large particles during transport from the source region to the measurement site. Furthermore, moderate linear correlations were found between PNC and CO, and total positive ions and CO (r = 0.69 and 0.62, respectively), indicating the impact of biomass burning on atmospheric particle number and ion concentrations in the study region (see **Figure S2**). To date, there has been a lack of research on ions from biomass burning emissions, and thus, further investigation is needed to explain these findings.

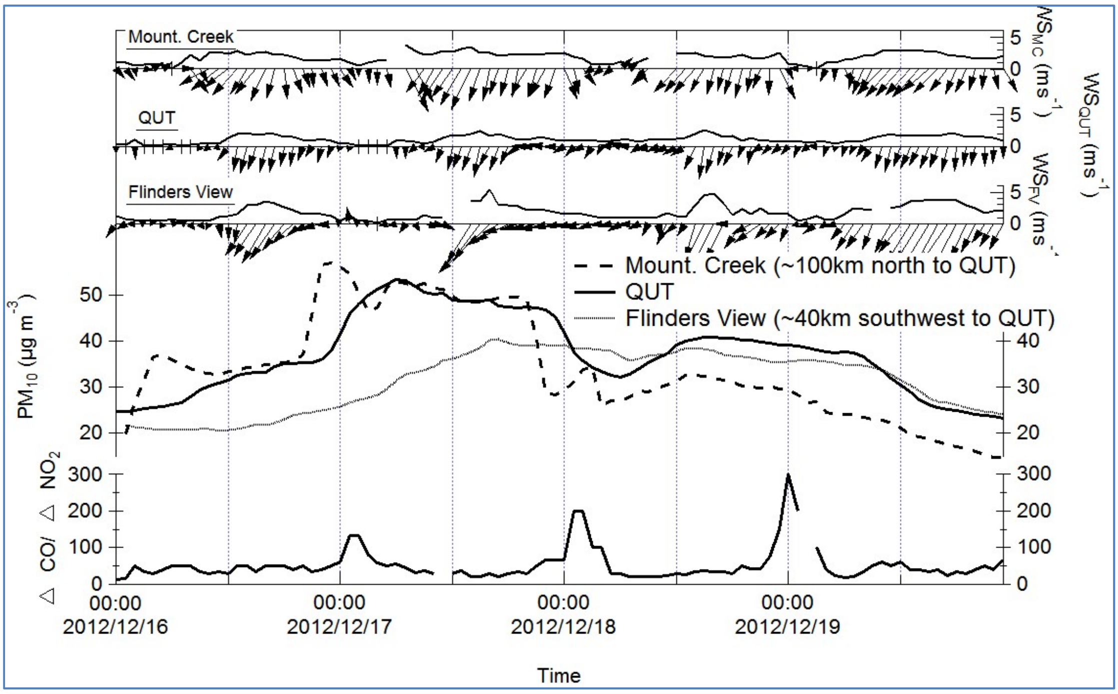

Figure 9. Time series of PM_{10} measured at Mount Creek (MC), QUT, and Flinders View (FV) and $\Delta CO/\Delta NO_2$ (QUT only) during the period of 16-19 December 2012 (bottom panel). Wind vector and wind speed were illustrated in upper panel.

4. Conclusions

Continuous measurements of atmospheric ion and particle number concentrations were conducted in an urban area of Brisbane, Australia during 3 to 19 December 2012. The median total ion and particle number concentrations were found to be (-1.2 x 10^3 cm^{-3} | +1.6 x 10^3 cm^{-3}) and 4.4 x 10^3 cm^{-3}, respectively, over the entire sampling period. Significant correlations were found between negative and positive cluster ions, which suggested that they were from similar sources. The correlation analysis between ion and nitrogen oxides concentrations showed that the influence of vehicle exhaust emissions on cluster ions was less significant than on intermediate and large ions in an urban environment. Cluster and intermediate ion concentrations did not show strong wind direction dependence compared to that of large ions, which implied that cluster and intermediate ions measured at this site were from natural sources rather than industrial/vehicular sources (which were mainly located in the northeast and southwest regions). Under the influence of NPF, the median total ion ($d \leq 42$ nm) concentrations were found to be (-1249 cm^{-3} | +1715 cm^{-3}) for event days, which were higher than that for non-event days (-1175 cm^{-3} | +1573 cm^{-3}). Diurnal variations of the ion concentrations on the NPF event and non-event days showed that intermediate and large ions increased during NPF events, indicating that they were involved in the particle formation process. Elevated total ions, especially larger ions, and PNC were found during the biomass burning episode, which probably showed the attachment of cluster ions on accumulation particles associated to the biomass burning emission, which were in turn transported to the measurement site. The results of this work strongly suggested that further studies are necessary to investigate the impact of biomass burning on the atmospheric ion budget in greater details.

Acknowledgment

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Supplementary material

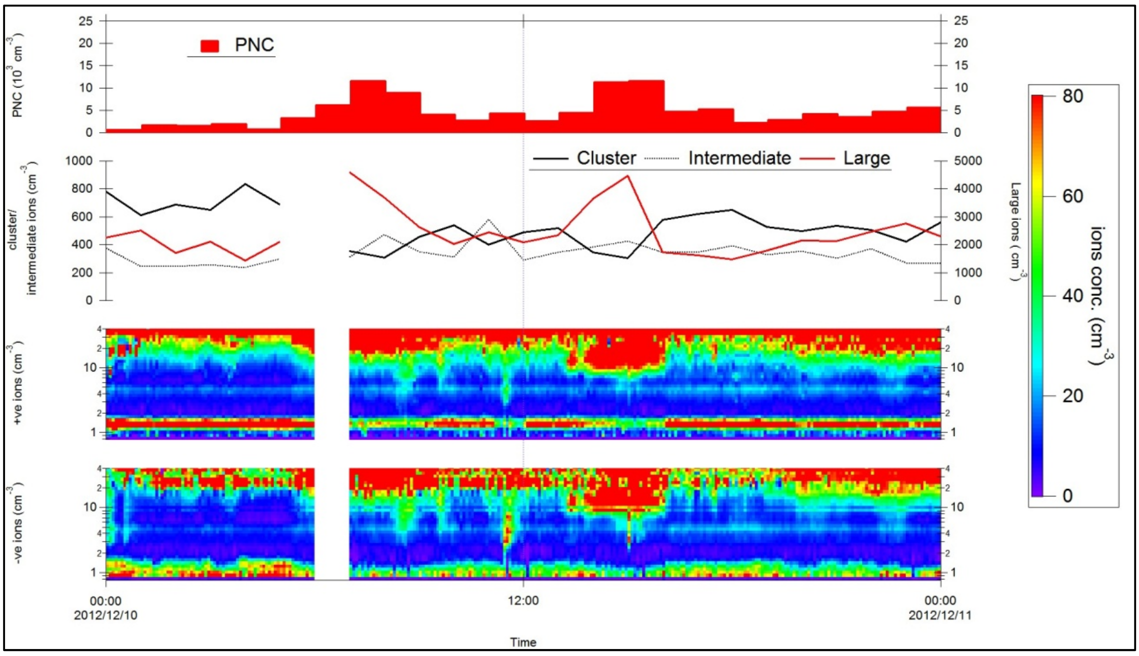

Figure S1. From bottom to top: time series of size distribution of i) negative and ii) positive ions and number concentrations of iii) cluster/ intermediate/ large ions and iv) PNC observed on 10 December 2012.

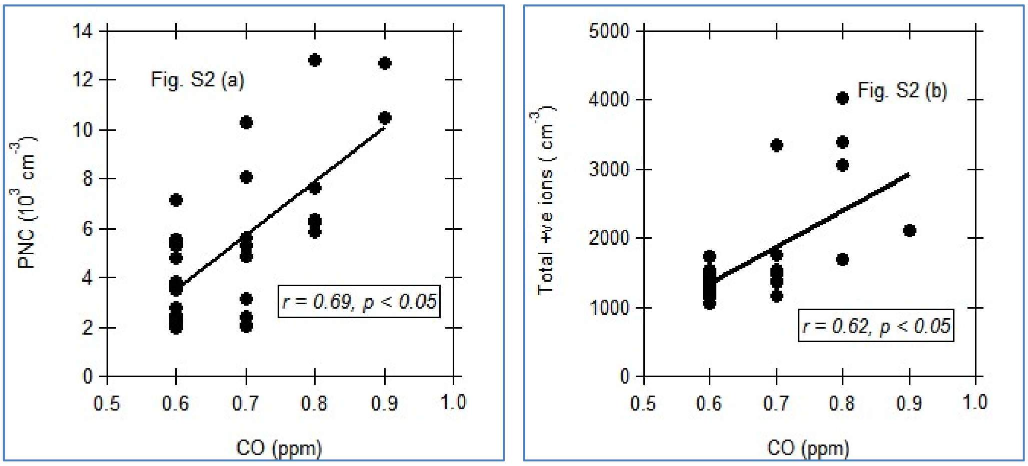

Figure S2. Scatter plot between a) PNC and b) total positive ions versus CO during nighttime of the period 16 – 19 December 2012.